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(51) Int.Cl.<sup>7</sup> C11D 3/386, C11D 7/54, C11D 7/42, C11D 3/395  
(30) 1999/11/24 (199 56 382.9) DE  
(54) **PROCEDE DE PREPARATION DE MICROCAPSULES  
D'ENZYMES**  
(54) **PROCESS FOR THE PREPARATION OF  
MICROENCAPSULATED ENZYMES**

(57) A process for the preparation of microencapsulated enzymes is claimed which comprises mixing together and dispersing a starch solution or starch emulsion and an enzyme solution. This process produces a preparation form for enzymes in which the enzymes are stabilized and which can be incorporated into detergents and cleaners without the enzyme activity being significantly reduced.

**Abstract**

A process for the preparation of microencapsulated enzymes is claimed which comprises mixing together and dispersing a starch solution or starch emulsion and an enzyme solution. This process produces a preparation form for enzymes in which the enzymes are stabilized and which can be incorporated into detergents and cleaners without the enzyme activity being significantly reduced.

**Process for the preparation of microencapsulated  
enzymes**

**Field of the Invention**

5 The present invention relates to a process for the preparation of microencapsulated enzymes, to the use of these enzymes in detergents and cleaners, and to a detergent and cleaner.

10 **Background of the Invention**

Enzymes for further industrial processing are generally supplied as liquid enzyme concentrates which are isolated from a fermentation broth and supplied in concentrated form. The stability of the enzymes in an aqueous environment is only limited. In order to  
15 convert the resulting enzyme concentrates into an anhydrous form, the concentrate can be spray dried e.g. in the presence of a polymeric binder, wherein the dried enzyme particles are taken up by the binder and aggregates form. To prepare liquid preparations, the  
20 spray-dried particles are redispersed.

A process for the preparation of enzyme dispersions is disclosed in WO 94/25560. The process described therein  
25 involves the emulsification of an enzyme preparation in a water-immiscible liquid in the presence of a polymeric dispersion stabilizer, forming a stable dispersion of the aqueous enzyme particles which, in the anhydrous state, have a particle size with a  
30 diameter of less than 30  $\mu\text{m}$ , and dehydration of the dispersed particles by azeotropic distillation. The essential feature of the process described is that, before, during or after the dehydration of the particles, an organic liquid, which is less volatile  
35 than the water-immiscible liquid and which is chosen from surfactants and water-miscible liquids, is added to the dispersion, and the water-immiscible liquid is distilled off from the dispersion until the amount of

this initially introduced water-immiscible liquid in the dispersion which remains is below 20% by weight, based on the liquid phase of the dispersion.

- 5 International patent application WO 97/24177 discloses a detergent concentrate suitable for dilution with water which consists of a liquid detergent phase and enzyme-containing particles dispersed therein. Here, at least 90% by weight of the enzyme-containing particles  
10 should have a diameter of less than 30  $\mu\text{m}$  and consist for their part of a shell prepared from a condensation polymer and permeable to water and compounds of low molecular weight, and of a core representing the enzyme component. The essential feature here is that the core  
15 does not itself consist only of enzyme, but also of a detergent phase which is in equilibrium with the surrounding liquid, and a core polymer where, in the moment when, for the preparation of the wash liquid, the claimed detergent concentrate is diluted with  
20 water, this water passes osmotically into the particle core and cooperates with the water which is already present therein in order to allow the particle to swell by at least 1.2-fold in diameter, as a result of which the enzyme is released into the wash water at the  
25 moment of dilution. This document thus concerns itself essentially with making possible a biophysically optimal release process. The actual enzyme formulation is secondary here.
- 30 The preparation of enzymes in pulverulent form, for example by spray drying or else by crystallization processes, frequently leads to very fine powders with particle sizes below 20  $\mu\text{m}$  which, because of the possible formation of dust, entails health risks as a  
35 result of the inhalation of the dust during preparation and processing. Added to this is the fact that in the case of these drying processes some of the enzymatic activity can be lost as a result of denaturation.

An important field of application for enzymes is detergents and cleaners. In these compositions, the enzymes are either incorporated as solid constituents  
5 or in the form of liquid formulations.

In the preparation of liquid detergents and cleaners, it is particularly advantageous and cost-effective if the starting materials are also present in liquid or  
10 dispersed form. For the use of the enzymes, the direct use of the enzyme concentrates obtained from the preparation presents itself. However, these concentrates have a relatively high water content. In liquid formulations there is also the danger that the enzymes  
15 will at least partially lose their activity.

Liquid bleach-containing formulations require the water content to be only low in order to stabilize the bleach. This means that the water content of the raw  
20 materials used must accordingly be low.

Accordingly, the object of the present invention was to provide a preparation form for enzymes in which the enzymes are stabilized and which can be incorporated  
25 into detergents and cleaners without the enzyme activity being significantly reduced.

Surprisingly, it has been found that enzymes can be stabilized in a simple manner by microencapsulating  
30 them using aqueous starch solutions or starch emulsions; they can then be added to the detergents and cleaners either as microemulsions or in the form of spray-dried products.

### 35 **Summary of the Invention**

The present invention provides, accordingly, a process for the preparation of microencapsulated enzymes which

comprises mixing together and dispersing a starch solution or starch emulsion and an enzyme solution.

#### **Detailed Description of the Invention**

5 For the preparation of microencapsulated enzymes or enzyme preparations, water-soluble or water-emulsifiable starches or starch derivatives, such as, for example, hydrophobicized starches, are suitable. Examples of such starch derivatives are maltodextrins,  
10 glucose syrups or dehydrated glucose or octenyl succinate starches. Suitable starches are available commercially e.g. under Narlex® ST2 (National Starch) or Cleargum CO 01® (Roquette).

15 The enzymes can be chosen from any enzymes customary for detergents and cleaners. Suitable enzymes are primarily the proteases, lipases, amylases and/or cellulases obtained from microorganisms, such as bacteria or fungi, preference being given to proteases  
20 derived and/or produced from *Bacillus* species, and to their mixtures with amylases. They are obtained from suitable microorganisms in a known manner by fermentation processes which are described, for example, in the German laid-open specifications  
25 DE 19 40 488, DE 20 44 161, DE 22 01 803 and DE 21 21 397, the US American patent specifications US 3 632 957 and US 4 264 738, the European patent application EP 006 638, and the International patent application WO 91/912792. If the preparation prepared  
30 in accordance with the invention is a protease-containing preparation, the protease activity is preferably 150 000 protease units (PU, determined in accordance with the method described in *Tenside [surfactants]*, vol. 7 (1970), pp. 125-132) to  
35 350 000 PU, in particular 160 000 PU to 300 000 PU, per gram of preparation.

The enzyme solutions are preferably used as enzyme concentrates, as can be obtained, for example, by processes known from the prior art, e.g. by micro-filtration or ultrafiltration. If the enzyme con-  
5 concentrates are protease concentrates, then the protease activity can amount to 1 500 000 PU.

To carry out the process according to the invention, a concentrated, aqueous enzyme solution and a starch  
10 solution are preferably firstly mixed with one another, and the enzyme solution is finely dispersed within the starch solution using a dispersion device. As a result of this process, the enzymes are surrounded by starch molecules and thereby stabilized.

15 The microencapsulated enzymes obtained according to the invention can be passed to their intended uses in the form of their dispersions or as concentrated products in a manner known per se and be further processed  
20 there.

If the microencapsulated enzymes are to be processed in solid form, then the water can be removed using processes known from the prior art, such as spray  
25 drying, centrifugation or by resolubilization. The particles obtained usually have a particle size between 50 and 200  $\mu\text{m}$ .

In a preferred embodiment the microencapsulated enzymes  
30 are used in detergents and cleaners.

The present invention, accordingly, further provides for the use of the microencapsulated enzymes obtained by the process described above in detergents and  
35 cleaners, preferably in liquid to gelatinous bleach-containing detergents and cleaners.

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The present invention also provides detergents and cleaners which comprise surfactants and builder substances, and optionally further customary ingredients, which are notable for the fact that they  
5 comprise microencapsulated enzymes as can be obtained by the process described above.

The compositions according to the invention comprise surfactants, e.g. nonionic, anionic and amphoteric  
10 surfactants, and bleaches, and optionally further customary ingredients.

The nonionic surfactants used are preferably alkoxyated, advantageously ethoxylated, in particular  
15 primary alcohols having, preferably, 8 to 18 carbon atoms and, on average, 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical can be linear or, preferably, methyl-branched in the 2-position, or can comprise linear and methyl-branched  
20 radicals in a mixture as are customarily present in oxo alcohol radicals. Particular preference is, however, given to alcohol ethoxylates containing linear radicals of alcohols of a native origin having 12 to 18 carbon atoms, e.g. from coconut, palm, tallow fatty or oleyl  
25 alcohol, and, on average, 2 to 8 EO per mole of alcohol. Preferred ethoxylated alcohols include, for example, C<sub>12-14</sub>-alcohols having 3 EO or 4 EO, C<sub>9-11</sub>-alcohol having 7 EO, C<sub>13-15</sub>-alcohols having 3 EO, 5 EO, 7 EO or 8 EO, C<sub>12-18</sub>-alcohols having 3 EO, 5 EO or  
30 7 EO and mixtures of these, such as mixtures of C<sub>12-14</sub>-alcohol with 3 EO and C<sub>12-18</sub>-alcohol having 5 EO. The degrees of ethoxylation given are statistical average values which can be an integer or a fraction for a specific product. Preferred alcohol ethoxylates  
35 have a narrowed homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols having more than 12 EO can



also be used. Examples thereof are tallow fatty alcohol having 14 EO, 25 EO, 30 EO or 40 EO.

5 A further class of preferred nonionic surfactants, which are used either as the sole nonionic surfactant or in combination with other nonionic surfactants, are alkoxyated, preferably ethoxyated or ethoxyated and propoxyated fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, in particular  
10 fatty acid methyl esters.

A further class of nonionic surfactants which can advantageously be used are the alkyl polyglycosides (APG). Alkyl polyglycosides which can be used satisfy  
15 the general formula  $RO(G)_z$  in which R is a linear or branched, in particular methyl-branched in the 2-position, saturated or unsaturated, aliphatic radical having 8 to 22, preferably 12 to 18 carbon atoms, and G is the symbol which stands for a glucose unit having 5  
20 or 6 carbon atoms, preferably for glucose. The degree of glycosylation z is here between 1.0 and 4.0, preferably between 1.0 and 2.0 and in particular between 1.1 and 1.4. Preference is given to using linear alkyl polyglucosides, i.e. alkyl polyglycosides  
25 in which the polyglycosyl radical is a glucose radical, and the alkyl radical is an n-alkyl radical.

Also, nonionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethylamine oxide and  
30 N-tallow alkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type may be suitable. The proportion of these nonionic surfactants is preferably no more than that of the ethoxyated fatty alcohols, in particular no more than half thereof.

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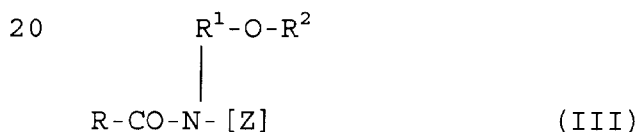
Further suitable surfactants are polyhydroxy fatty acid amides of the formula (II)

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5 in which RCO is an aliphatic acyl radical having 6 to  
22 carbon atoms,  $\text{R}^1$  is hydrogen, an alkyl or  
hydroxyalkyl radical having 1 to 4 carbon atoms and [Z]  
is a linear or branched polyhydroxyalkyl radical having  
3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The  
10 polyhydroxy fatty acid amides are known substances  
which can usually be obtained by reductive amination of  
a reducing sugar with ammonia, an alkylamine or an  
alkanolamine and subsequent acylation with a fatty  
acid, a fatty acid alkyl ester or a fatty acid  
15 chloride.

The group of polyhydroxy fatty acid amides also  
includes compounds of the formula (III)



in which R is a linear or branched alkyl or alkenyl  
25 radical having 7 to 12 carbon atoms,  $\text{R}^1$  is a linear,  
branched or cyclic alkyl radical or an aryl radical  
having 2 to 8 carbon atoms, and  $\text{R}^2$  is a linear,  
branched or cyclic alkyl radical or an aryl radical or  
an oxy-alkyl radical having 1 to 8 carbon atoms, where  
30  $\text{C}_{1-4}$ -alkyl or phenyl radicals are preferred, and [Z] is  
a linear polyhydroxyalkyl radical whose alkyl chain is  
substituted by at least two hydroxyl groups, or  
alkoxylated, preferably ethoxylated or propoxylated,  
derivatives of this radical.

35

[Z] is preferably obtained by reductive amination of a  
reducing sugar, for example glucose, fructose, maltose,  
lactose, galactose, mannose or xylose. The N-alkoxy- or

N-aryloxy-substituted compounds can then be converted, for example by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, into the desired polyhydroxy fatty acid amides.

5

The surfactants may be present in the cleaners or detergents according to the invention in an overall amount of from preferably 5% by weight to 50% by weight, in particular from 8% by weight to 30% by weight, based on the finished composition.

10

The anionic surfactants used are, for example, those of the sulfonate and sulfate type. Suitable surfactants of the sulfonate type are, preferably, C<sub>9-13</sub>-alkylbenzenesulfonates, olefin sulfonates, i.e. mixtures of alkene- and hydroxyalkanesulfonates, and disulfonates, as obtained, for example, from C<sub>12-18</sub>-monoolefins having a terminal or internal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Also suitable are alkanesulfonates, which are obtained from C<sub>12-18</sub>-alkanes, for example by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization. Likewise suitable are also the esters of  $\alpha$ -sulfo fatty acids (ester sulfonates), e.g. the  $\alpha$ -sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids.

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25

Further suitable anionic surfactants are sulfated fatty acid glycerol esters. Fatty acid glycerol esters is understood as meaning the mono-, di- and triesters, and mixtures thereof, as are obtained during the preparation by esterification of a monoglycerol with 1 to 3 mol of fatty acid or during the transesterification of triglycerides with 0.3 to 2 mol of glycerol. Preferred sulfated fatty acid glycerol esters are here the sulfation products of saturated fatty acids having 6 to 22 carbon atoms, for example of

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caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

5 Preferred alk(en)yl sulfates are the alkali metal, and in particular the sodium, salts of sulfuric half-esters of C<sub>12-18</sub>-fatty alcohols, for example coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol or of C<sub>10-20</sub>-oxo alcohols and those  
10 half-esters of secondary alcohols of these chain lengths. Further preferred are alk(en)yl sulfates of said chain length which comprise a synthetic, petroleum-based straight-chain alkyl radical which have analogous degradation behavior to the equivalent  
15 compounds based on fatty chemical raw materials. From a washing performance viewpoint, preference is given to C<sub>12-C16</sub>-alkyl sulfates and C<sub>12-C15</sub>-alkyl sulfates, and C<sub>14-C15</sub>-alkyl sulfates. 2,3-Alkyl sulfates are also suitable anionic surfactants.

20

The sulfuric monoesters of straight-chain or branched C<sub>7-21</sub>-alcohols ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl-branched C<sub>9-11</sub>-alcohols having, on average, 3.5 mol of ethylene oxide (EO) or  
25 C<sub>12-18</sub>-fatty alcohols having 1 to 4 EO, are also suitable. Because of their high foaming behavior, they are used in cleaners only in relatively small amounts, for example in amounts up to 5% by weight, usually from 1 to 5% by weight.

30

Further suitable anionic surfactants are also the salts of alkylsulfosuccinic acid, which are also referred to as sulfosuccinates or as sulfosuccinic esters and which represent monoesters and/or diesters of sulfosuccinic  
35 acid with alcohols, preferably fatty alcohols and, in particular, ethoxylated fatty alcohols. Preferred sulfosuccinates contain C<sub>8-18</sub>-fatty alcohol radicals or mixtures thereof. In particular, preferred sulfo-

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succinates contain a fatty alcohol radical derived from ethoxylated fatty alcohols, which are themselves nonionic surfactants (see below for description). In this connection, sulfosuccinates whose fatty alcohol radicals are derived from ethoxylated fatty alcohols having a narrowed homolog distribution are, in turn, particularly preferred. Likewise, it is also possible to use alk(en)ylsuccinic acid having, preferably, 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof.

Further suitable anionic surfactants are, in particular, soaps. Saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and, in particular, soap mixtures derived from natural fatty acids, e.g. coconut, palm kernel or tallow fatty acids, are suitable.

The anionic surfactants including the soaps may be present in the form of their sodium, potassium or ammonium salts, and as soluble salts of organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably in the form of their sodium or potassium salts, in particular in the form of the sodium salts.

Of the compounds which serve as bleaches and produce  $H_2O_2$  in water, sodium perborate tetrahydrate and sodium perborate monohydrate are of particular importance. Other bleaches which can be used are, for example, sodium percarbonate, peroxyphosphates, citrate perhydrates, and  $H_2O_2$ -producing peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoperacid or diperdodecanedioic acid. If bleaches are used it is also possible to dispense with the use of surfactants and/or builders, meaning that pure bleach tablets can

be prepared. If such bleach tablets are to be used for textile washing, a combination of sodium percarbonate with sodium sesquicarbonate is preferred, irrespective of which further ingredients are present in the moldings. If cleaner or bleach tablets for machine dishwashing are prepared, then it is also possible to use bleaches from the group of organic bleaches. Typical organic bleaches are diacyl peroxides, such as, for example, dibenzoyl peroxide. Further typical organic bleaches are the peroxy acids, specific examples being alkylperoxy acids and arylperoxy acids. Preferred representatives are (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, but also peroxy- $\alpha$ -naphthoic acid and magnesium monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxyauric acid, peroxysearic acid, 8-phthalimidoperoxycaproic acid [phthalimidoperoxylhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxy-carboxylic acid, 1,9-diperoxyazelaic acid, diperoxy-sebacic acid, diperoxybrassylic acid, diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyldi(6-aminopercaproic acid).

In order to achieve improved bleaching action in cases of washing at temperatures of 60°C and below, and in particular in the case of laundry pretreatment, bleach activators can be incorporated into the detergent and cleaner moldings. Bleach activators which can be used are compounds which, under perhydrolysis conditions, give aliphatic peroxocarboxylic acids having, preferably, 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or optionally substituted perbenzoic acid. Substances which carry O- and/or N-acyl groups of said number of carbon atoms and/or

optionally substituted benzoyl groups are suitable. Preference is given to polyacylated alkylenediamines, in particular tetraacetylenediamine (TAED), acylated triazine derivatives, in particular  
5 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular 1,3,4,6-tetraacetylglycoluril (TAGU), N-acylimides, in particular N-nonanoysuccinimide (NOSI), acylated phenolsulfonates, in particular n-nonanoyl- or  
10 isononanoxyloxybenzenesulfonate (n- or iso-NOBS), acylated hydroxycarboxylic acids, such as triethyl O-acetylcitrate (TEOC), carboxylic anhydrides, in particular phthalic anhydride, isatoic anhydride and/or succinic anhydride, carboxamides, such as  
15 N-methyldiacetamide, glycolide, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate, isopropenyl acetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from German patent applications DE 196 16 693 and DE 196 16 767,  
20 and acetylated sorbitol and mannitol, or mixtures thereof described in European patent application EP 0 525 239 (SORMAN), acylated sugar derivatives, in particular pentaacetylglucose (PAG), pentaacetylfructose, tetraacetylxylose and  
25 octaacetyllactose, and acetylated, optionally N-alkylated glucamine or gluconolactone, triazole or triazole derivatives and/or particulate caprolactams and/or caprolactam derivatives, preferably N-acylated lactams, for example N-benzoylcaprolactam and  
30 N-acetylcaprolactam, which are known from International patent applications WO-A-94/27970, WO-A-94/28102, WO-A-94/28103, WO-A-95/00626, WO-A-95/14759 and WO-A-95/17498. The hydrophilically substituted acylacetals known from German patent application  
35 DE-A-196 16 769 and the acyllactams described in German patent application DE-A-196 16 770 and International patent application WO-A-95/14075 are likewise used with preference. It is also possible to use the combinations

of conventional bleach activators known from German patent application DE-A-44 43 177. Nitrile derivatives, such as cyanopyridines, nitrile quats, e.g. N-alkylammoniumacetonitriles, and/or cyanamide derivatives can also be used. Preferred bleach activators are sodium 4-(octanoyloxy)benzenesulfonate, *n*-nonanoyl or isononanoyloxybenzenesulfonate (*n*- or iso-NOBS), undecenoyloxybenzenesulfonate (UDOBS), sodium dodecanoyloxybenzenesulfonate (DOBS), decanoyloxybenzoic acid (DOBA, OBC 10) and/or dodecanoyloxybenzenesulfonate (OBS 12), and N-methylmorpholiniumacetonitrile (MMA). Such bleach activators can be present in the customary quantitative range from 0.01 to 20% by weight, preferably in amounts from 0.1 to 15% by weight, in particular 1% by weight to 10% by weight, based on the total composition.

In addition to the conventional bleach activators or instead of them, it is also possible for so-called bleach catalysts to be present. These substances are bleaching-enhancing transition metal salts or transition metal complexes, such as, for example, Mn, Fe, Co, Ru or Mo salene complexes or carbonyl complexes. Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes containing N-containing tripod ligands, and Co, Fe, Cu and Ru ammine complexes are also suitable as bleach catalysts, preference being given to using those compounds described in DE 197 09 284 A1.

The content of bleaches in the compositions can be 1 to 40% by weight and in particular 10 to 20% by weight, perborate monohydrate or percarbonate being used advantageously.

The compositions according to the invention generally comprise one or more builders, in particular zeolites, silicates, carbonates, organic cobuilders and - where no ecological grounds oppose their use - also



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phosphates. The latter are the preferred builders in particular in detergent tablets for machine dishwashing.

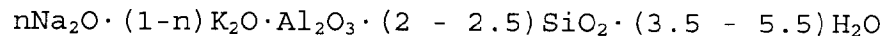
- 5 Suitable crystalline, layered sodium silicates have the general formula  $\text{NaMSi}_x\text{O}_{2x+1}\cdot\text{H}_2\text{O}$ , where M is sodium or hydrogen, x is a number from 1.9 to 4, and y is a number from 0 to 20, and preferred values for x are 2, 3 or 4. Preferred crystalline phyllosilicates of the  
10 given formula are those in which M is sodium and x assumes the values 2 or 3. In particular, both  $\beta$ - and also  $\delta$ -sodium disilicates  $\text{Na}_2\text{Si}_2\text{O}_5\cdot y\text{H}_2\text{O}$  are preferred.

It is also possible to use amorphous sodium silicates  
15 having an  $\text{Na}_2\text{O}:\text{SiO}_2$  modulus of from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8 and in particular from 1:2 to 1:2.6, which have delayed dissolution and secondary detergent properties. The dissolution delay relative to  
20 conventional amorphous sodium silicates can have been induced by various means, for example by surface treatment, compounding, compaction/compression or by overdrying. Within the scope of this invention, the term "amorphous" also includes "X-ray amorphous". This means that in X-ray diffraction experiments the  
25 silicates do not give the sharp X-ray reflections typical of crystalline substances, but instead, at best, one or more maxima of the scattered X-rays having a breadth of several degree units of the diffraction angle. However, particularly good builder properties  
30 will very likely result if in electron diffraction experiments the silicate particles give poorly defined or even sharp diffraction maxima. This is to be interpreted to the effect that the products have microcrystalline regions with a size from 10 to a few  
35 hundred nm, preference being given to values up to at most 50 nm and in particular up to at most 20 nm. Particular preference is given to compressed/compacted

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amorphous silicates, compounded amorphous silicates and overdried X-ray amorphous silicates.

The finely crystalline, synthetic zeolite containing  
 5 bonded water used is preferably zeolite A and/or P. As  
 zeolite P, zeolite MAP<sup>®</sup> (commercial product from  
 Crosfield) is particularly preferred. However,  
 zeolite X, and mixtures of A, X and/or P are also  
 suitable. A product which is commercially available and  
 10 can be used with preference within the scope of the  
 present invention is, for example, also a co-  
 crystallizate of zeolite X and zeolite A (approximately  
 80% by weight of zeolite X), which is sold by CONDEA  
 Augusta S.p.A. under the trade name VEGOBOND AX<sup>®</sup> and  
 15 can be described by the formula



Suitable zeolites have an average particle size of less  
 20 than 10  $\mu\text{m}$  (volume distribution; measurement method:  
 Coulter counter) and preferably contain 18 to 22% by  
 weight, in particular 20 to 22% by weight, of bonded  
 water.

25 A use of the generally known phosphates as builder  
 substances is of course also possible, provided such a  
 use is not to be avoided for ecological reasons. Among  
 the large number of commercially available phosphates,  
 the alkali metal phosphates are of the greatest  
 30 significance in the detergents and cleaners industry,  
 especially pentasodium or pentapotassium triphosphate  
 (sodium or potassium tripolyphosphate).

Here, alkali metal phosphates is the collective term  
 35 for the alkali metal (in particular sodium and  
 potassium) salts of various phosphoric acids, it being  
 possible to differentiate between metaphosphoric acids  
 $(\text{HPO}_3)_n$  and orthophosphoric acid  $\text{H}_3\text{PO}_4$ , as well as

higher molecular weight representatives. The phosphates combine several advantages: they act as alkali carriers, prevent lime deposits on machine parts and lime incrustations in fabrics and moreover contribute  
5 to the cleaning performance.

Sodium dihydrogenphosphate,  $\text{NaH}_2\text{PO}_4$ , exists as dihydrate (density  $1.91 \text{ gcm}^{-3}$ , melting point  $60^\circ$ ) and as monohydrate (density  $2.04 \text{ gcm}^{-3}$ ). Both salts are white  
10 powders which are very readily soluble in water and which lose their water of crystallization upon heating and at  $200^\circ\text{C}$  convert to the weakly acidic diphosphate (disodium hydrogendiphosphate,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ), at a higher temperature into sodium trimetaphosphate ( $\text{Na}_3\text{P}_3\text{O}_9$ ) and  
15 Maddrell's salt (see below).  $\text{NaH}_2\text{PO}_4$  is acidic; it forms when phosphoric acid is adjusted to a pH of 4.5 using sodium hydroxide solution and the suspension is sprayed. Potassium dihydrogenphosphate (primary or monobasic potassium phosphate, potassium biphosphate, KDP),  $\text{KH}_2\text{PO}_4$ , is a white salt of density  $2.33 \text{ gcm}^{-3}$ , has  
20 a melting point of  $253^\circ$  [decomposition with the formation of potassium polyphosphate  $(\text{KPO}_3)_x$ ] and is readily soluble in water.

25 Disodium hydrogenphosphate (secondary sodium phosphate),  $\text{Na}_2\text{HPO}_4$ , is a colorless crystalline salt which is very readily soluble in water. It exists in anhydrous form and with 2 mol of water (density  $2.066 \text{ gcm}^{-3}$ , water loss at  $95^\circ$ ), 7 mol of water (density  
30  $1.68 \text{ gcm}^{-3}$ , melting point  $48^\circ$  with loss of 5  $\text{H}_2\text{O}$ ) and 12 mol of water (density  $1.52 \text{ gcm}^{-3}$ , melting point  $35^\circ$  with loss of 5  $\text{H}_2\text{O}$ ), becomes anhydrous at  $100^\circ$  and upon more vigorous heating converts to the diphosphate  $\text{Na}_4\text{P}_2\text{O}_7$ . Disodium hydrogenphosphate is prepared by  
35 neutralizing phosphoric acid with soda solution using phenolphthalein as indicator. Dipotassium hydrogenphosphate (secondary or dibasic potassium phosphate),

$K_2HPO_4$ , is an amorphous, white salt which is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate,  $Na_3PO_4$ ,  
5 are colorless crystals which in the form of the dodecahydrate have a density of  $1.62 \text{ gcm}^{-3}$  and a melting point of  $73-76^\circ\text{C}$  (decomposition), in the form of the decahydrate (corresponding to 19-20% of  $P_2O_5$ ) have a  
10 melting point of  $100^\circ\text{C}$  and in anhydrous form (corresponding to 39-40% of  $P_2O_5$ ) have a density of  $2.536 \text{ gcm}^{-3}$ . Trisodium phosphate is readily soluble in water with an alkaline reaction and is prepared by evaporating a solution of exactly 1 mol of disodium phosphate and 1 mol of NaOH. Tripotassium phosphate  
15 (tertiary or tribasic potassium phosphate),  $K_3PO_4$ , is a white, deliquescent granular powder of density  $2.56 \text{ gcm}^{-3}$ , has a melting point of  $1340^\circ$  and is readily soluble in water with an alkaline reaction. It is produced, for example, during the heating of Thomas  
20 slag with carbon and potassium sulfate. Despite the higher price, the more readily soluble, and therefore highly effective, potassium phosphates are often preferred over corresponding sodium compounds in the detergents industry.

25 Tetrasodium diphosphate (sodium pyrophosphate),  $Na_4P_2O_7$ , exists in anhydrous form (density  $2.534 \text{ gcm}^{-3}$ , melting point  $988^\circ$ , also  $880^\circ$  given) and as decahydrate (density  $1.815-1.836 \text{ gcm}^{-3}$ , melting point  $94^\circ$  with loss  
30 of water). Both substances are colorless crystals which dissolve in water with an alkaline reaction.  $Na_4P_2O_7$  is formed during the heating of disodium phosphate to  $> 200^\circ$  or by reacting phosphoric acid with soda in a stoichiometric ratio and dewatering the solution by  
35 spraying. The decahydrate complexes heavy metal salts and hardness constituents and thus reduces the hardness of the water. Potassium diphosphate (potassium pyrophosphate),  $K_4P_2O_7$ , exists in the form of the trihydrate

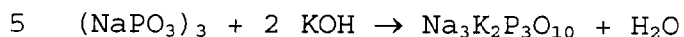
and is a colorless, hygroscopic powder having a density of  $2.33 \text{ g cm}^{-3}$ , which is soluble in water, the pH of the 1% strength solution at  $25^\circ$  being 10.4.

- 5 By condensing  $\text{NaH}_2\text{PO}_4$  or  $\text{KH}_2\text{PO}_4$ , higher molecular weight sodium and potassium phosphates are formed, amongst which cyclic representatives, the sodium or potassium metaphosphates, and chain-shaped types, the sodium or potassium polyphosphates, can be differentiated.
- 10 Particularly for the latter, a large number of names are in use: melt or thermal phosphates, Graham's salt, Kurrol's and Maddrell's salt. All higher sodium and potassium phosphates are commonly referred to as condensed phosphates.

15

- The industrially important pentasodium triphosphate,  $\text{Na}_5\text{P}_3\text{O}_{10}$  (sodium tripolyphosphate), is a nonhygroscopic, white, water-soluble salt which is anhydrous or crystallizes with 6  $\text{H}_2\text{O}$  and is of the general formula
- 20  $\text{NaO}-[\text{P}(\text{O})(\text{ONa})-\text{O}]_n-\text{Na}$  where  $n = 3$ . In 100 g of water, about 17 g of the salt which is free of water of crystallization dissolve at room temperature, about 20 g dissolve at  $60^\circ$ , and about 32 g dissolve at  $100^\circ$ ; if the solution is heated at  $100^\circ$  for two hours, about
- 25 8% of orthophosphate and 15% of diphosphate form as a result of hydrolysis. In the preparation of pentasodium triphosphate, phosphoric acid is reacted with soda solution or sodium hydroxide solution in a stoichiometric ratio, and the solution is dewatered by
- 30 spraying. Similarly to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves many insoluble metal compounds (including lime soaps etc.). Pentapotassium triphosphate,  $\text{K}_5\text{P}_3\text{O}_{10}$  (potassium tripolyphosphate), is available commercially, for example, in
- 35 the form of a 50% strength by weight solution ( $> 23\%$  of  $\text{P}_2\text{O}_5$ ,  $25\%$  of  $\text{K}_2\text{O}$ ). The potassium polyphosphates are used widely in the detergents and cleaners industry. In addition, sodium potassium tripolyphosphates also exist

which can likewise be used within the scope of the present invention. These arise, for example, when sodium trimetaphosphate is hydrolyzed with KOH:



According to the invention, these can be used exactly as sodium tripolyphosphate, potassium tripolyphosphate or mixtures of the two; mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate or  
10     mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphosphate can also be used  
15     according to the invention.

Organic cobuilders which can be used in the detergent and cleaner moldings according to the invention are, in particular, polycarboxylates/polycarboxylic acids,  
20     polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, further organic cobuilders (see below), and phosphonates. These classes of substance are described below.

25     Organic builder substances which can be used are, for example, the polycarboxylic acids usable in the form of their sodium salts, the term polycarboxylic acids meaning those carboxylic acids which carry more than one acid function. Examples of these are citric acid,  
30     adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), provided such a use is not objectionable on ecological grounds, and mixtures thereof. Preferred salts are the  
35     salts of the polycarboxylic acids such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

The acids per se may also be used. In addition to their builder action, the acids typically also have the property of an acidifying component and thus also serve to establish a lower and milder pH of detergents or  
5 cleaners. In this connection, particular mention is made of citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any mixtures thereof.

Also suitable as builders are polymeric polycarboxylates; these are, for example, the alkali metal  
10 salts of polyacrylic acid or of polymethacrylic acid, for example those having a relative molecular mass of from 500 to 70 000 g/mol.

15 The molar masses given for polymeric polycarboxylates are, for the purposes of this specification, weight-average molar masses,  $M_w$ , of the respective acid form, determined fundamentally by means of gel permeation chromatography (GPC) using a UV detector. The measure-  
20 ment was made against an external polyacrylic acid standard which, owing to its structural similarity to the polymers under investigation, provides realistic molecular weight values. These figures differ considerably from the molecular weight values obtained  
25 using polystyrenesulfonic acids as the standard. The molar masses measured against polystyrenesulfonic acids are usually considerably higher than the molar masses given in this specification.

30 Suitable polymers are, in particular, polyacrylates which preferably have a molecular mass of from 2000 to 20 000 g/mol. Owing to their superior solubility, preference in this group may be given in turn to the short-chain polyacrylates which have molar masses of  
35 from 2000 to 10 000 g/mol and particularly preferably from 3000 to 5000 g/mol.

Also suitable are copolymeric polycarboxylates, in particular those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Copolymers which have proven to be particularly  
5 suitable are those of acrylic acid with maleic acid which contain from 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid. Their relative molecular mass, based on free acids, is generally 2000 to 70 000 g/mol, preferably 20 000 to 50 000 g/mol and  
10 in particular 30 000 to 40 000 g/mol.

The (co)polymeric polycarboxylates can either be used as powders or as aqueous solutions. The (co)polymeric polycarboxylate content of the compositions can be from  
15 0.5 to 20% by weight, in particular 3 to 10% by weight.

To improve the solubility in water, the polymers can also contain allylsulfonic acids, such as, for example, allyloxybenzenesulfonic acid and methallylsulfonic  
20 acid, as monomer.

Particular preference is also given to biodegradable polymers of more than two different monomer units, for example those which contain, as monomers, salts of  
25 acrylic acid and of maleic acid, and vinyl alcohol or vinyl alcohol derivatives, or those which contain, as monomers, salts of acrylic acid and of 2-alkylallyl-sulfonic acid, and sugar derivatives.

30 Further preferred copolymers are those which preferably have, as monomers, acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate.

Further preferred builder substances which may be  
35 mentioned are also polymeric aminodicarboxylic acids, their salts or their precursor substances. Particular preference is given to polyaspartic acids or salts and derivatives thereof.



Further suitable builder substances are polyacetals, which can be obtained by reacting dialdehydes with polyolcarboxylic acids which have 5 to 7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyolcarboxylic acids such as gluconic acid and/or glucoheptonic acid.

10

Further suitable organic builder substances are dextrans, examples being oligomers or polymers of carbohydrates, which can be obtained by partial hydrolysis of starches. The hydrolysis can be carried out by customary processes, for example acid-catalyzed or enzyme-catalyzed processes. The hydrolysis products preferably have average molar masses in the range from 400 to 500 000 g/mol. Preference is given here to a polysaccharide having a dextrose equivalent (DE) in the range from 0.5 to 40, in particular from 2 to 30, where DE is a common measure of the reducing effect of a polysaccharide compared with dextrose, which has a DE of 100. It is possible to use maltodextrans having a DE between 3 and 20 and dried glucose syrups having a DE between 20 and 37, and also so-called yellow dextrans and white dextrans with higher molar masses in the range from 2000 to 30 000 g/mol.

The oxidized derivatives of such dextrans are their reaction products with oxidizing agents which are able to oxidize at least one alcohol function of the saccharide ring to the carboxylic acid function. A product oxidized on the C<sub>6</sub> of the saccharide ring may be particularly advantageous.

35

Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are also further suitable cobuilders. Here, ethylenediamine

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N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. In this connection further preference is also given to glycerol disuccinates and glycerol trisuccinates. Suitable use  
5 amounts in zeolite-containing and/or silicate-containing formulations are 3 to 15% by weight.

Further organic cobuilders which can be used are, for example, acetylated hydroxycarboxylic acids or salts  
10 thereof, which may also be present in lactone form and which contain at least 4 carbon atoms and at least one hydroxyl group and at most two acid groups.

A further class of substance having cobuilder  
15 properties is the phosphonates. These are, in particular, hydroxyalkane- and aminoalkanephosphonates. Among the hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphate (HEDP) is of particular importance as a cobuilder. It is preferably used as sodium salt, the  
20 disodium salt being neutral and the tetrasodium salt being alkaline (pH 9). Suitable aminoalkanephosphonates are preferably ethylenediaminetetramethylenephosphonate (EDTMP), diethylenetriaminepentamethylenephosphonate (DTPMP) and higher homologs thereof. They are  
25 preferably used in the form of the neutral sodium salts, e.g. as the hexasodium salt of EDTMP or as the hepta- and octasodium salt of DTPMP. Here, preference is given to using HEDP as builder from the class of phosphonates. In addition, the aminoalkanephosphonates  
30 have a marked heavy-metal-binding capacity. Accordingly, particularly if the compositions also contain bleaches, it may be preferable to use aminoalkanephosphonates, in particular DTPMP, or mixtures of said phosphonates.

35

Moreover, all compounds which are able to form complexes with alkaline earth metal ions can be used as cobuilders.

In a preferred embodiment, the detergents and cleaners according to the invention are liquid to gelatinous compositions.

5 Solvents which can be used in the liquid to gelatinous compositions are, for example, from the group of monohydric or polyhydric alcohols, alkanolamines or glycol ethers, provided they are miscible with water in  
10 the given concentration range. Preferably, the solvents are chosen from ethanol, n- or i-propanol, butanols, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether,  
15 diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol monomethyl or monoethyl ether, diisopropylene glycol monomethyl or monoethyl ether, methoxy-, ethoxy- or butoxytriglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol,  
20 propylene glycol t-butyl ether, and mixtures of these solvents. Solvents can be used in the liquid to gelatinous detergents according to the invention in amounts between 0.1 and 20% by weight, but preferably below 15% by weight and in particular below 10% by  
25 weight.

To adjust the viscosity, one or more thickeners or thickening systems can be added to the composition according to the invention. The viscosity of the  
30 compositions according to the invention can be measured using customary standard methods (for example Brookfield viscometer RVD-VII at 20 rpm and 20°C, spindle 3) and is preferably in the range from 100 to 5000 mPas. Preferred compositions have viscosities of  
35 from 200 to 4000 mPas, values between 400 and 2000 mPas being particularly preferred.

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Suitable thickeners are inorganic or polymeric organic compounds. These mostly organic high molecular weight substances, which are also called swell(ing) agents, in most cases soak up the liquids and swell in the process, converting ultimately into viscous true or colloidal solutions.

Inorganic thickeners include, for example, polysilicic acids, clay minerals, such as montmorillonites, zeolites, silicas and bentonites.

The organic thickeners are from the groups of natural polymers, modified natural polymers or completely synthetic polymers.

Natural polymers which are used as thickeners are, for example, agar agar, carageen, tragacanth, gum arabic, alginates, pectins, polyoses, guar flour, carob seed grain, starch, dextrans, gelatins and casein.

Modified natural substances are primarily from the group of modified starches and celluloses. Examples which may be mentioned here are carboxymethylcellulose and other cellulose ethers, hydroxyethylcellulose and hydroxypropylcellulose, and carob flour ether.

A large group of thickeners which are used widely in very different fields of application are the completely synthetic polymers, such as polyacrylic and polymethacrylic compounds, vinyl polymers, polycarboxylic acids, polyethers, polyimines, polyamides and polyurethanes.

The thickeners may be present in an amount up to 5% by weight, preferably from 0.05 to 2% by weight, and particularly preferably from 0.1 to 1.5% by weight, based on the finished composition.

The detergent or cleaner according to the invention can comprise, as further customary ingredients, in particular sequestering agents, electrolytes, pH regulators, phosphonates, enzymes and further auxiliaries, such as optical brighteners, anti-redeposition agents, color-transfer inhibitors, foam regulators, additional bleach activators, dyes and fragrances.

10 For use in machine washing processes it may be advantageous to add customary foam inhibitors to the compositions. Suitable foam inhibitors are, for example, soaps of natural or synthetic origin which have a high proportion of C<sub>18</sub>-C<sub>24</sub>-fatty acids. Suitable  
15 nonsurfactant foam inhibitors are, for example, organopolysiloxanes and mixtures thereof with microfine, optionally silanized silica, and paraffin, waxes, microcrystalline waxes and mixtures thereof with silanized silica or bistearylethylenediamide. It is  
20 also advantageous to use mixtures of different foam inhibitors, e.g. those of silicones, paraffins or waxes. The foam inhibitors, in particular silicone- or paraffin-containing foam inhibitors, are preferably attached to a granular, water-soluble or water-  
25 dispersible carrier substance. Particular preference is given here to mixtures of paraffins and bistearyl-ethylenediamides.

As salts of polyphosphonic acids, preference is given  
30 to using the neutral sodium salts of, for example, 1-hydroxyethane-1,1-diphosphonate, diethylenetriamine-pentamethylenephosphonate or ethylenediaminetetramethylenephosphonate, which can be used in amounts of from 0.1 to 1.5% by weight.

35

The compositions according to the invention can comprise, as optical brighteners, derivatives of diaminostilbenedisulfonic acid or alkali metal salts

thereof. Suitable are e.g. salts of 4,4'-bis(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)stilbene-2,2'-disulfonic acid or similarly constructed compounds which carry a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. In addition, brighteners of the substituted diphenylstyryl type may be present, e.g. the alkali metal salts of 4,4'-bis(2-sulfostyryl)diphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)diphenyl. Mixtures of the above-mentioned brighteners can also be used.

If the composition according to the invention is used as a so-called liquid to gelatinous detergent, it preferably comprises from 0 to 20% by weight of anionic surfactants, 40 to 80% by weight of nonionic surfactants, 2 to 25% by weight of builder materials, 0 to 20% by weight of bleaches, 0 to 20% by weight of bleach activators, 0 to 5% by weight of enzymes, fragrances and further ingredients.

Example

For the preparation of microemulsions, starch was dissolved in water. After the starch had swelled, a  
 5 protease solution with an activity of 800 000 PU/g was added. The enzyme solution was then finely dispersed within the starch solution using a dispersion apparatus (Dispax® from IKA).

10 Table 1

	Micro-emulsion 1	Micro-emulsion 2	Untreated enzyme concentrate
Enzyme	Protease	Protease	Protease
Composition (%): Narlex® ST 2 starch (Manufacturer: National Starch)	44	36	0
Water from starch solution	30	24	0
Protease concentrate	26	40	100
Viscosity (mPas)	4300	2900	100
Use amount (%) in the Persil Kraftgel® liquid detergent (Manufacturer: Henkel KgaA)	0.4	0.26	0.15
Protease concentrate amount (%) in the liquid detergent	0.10	0.10	0.15

The enzyme stability in the liquid detergent was tested in a test under intensified conditions (temperature  
 15 60°C) in order to simulate realistic aging.

As Table 2 shows, both microemulsions displayed significant stability advantages over the untreated

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protease concentrate. For microemulsion 1, no decrease at all in the enzyme activity was detected. For microemulsion 2, the activity loss was less than 10%. By contrast, the untreated enzyme sample had an activity loss of 25-30%.

It was therefore found that the microencapsulated enzymes obtained according to the invention have good stability. In particular, no delayed protein precipitations were observed, as is often the case with the enzyme preparations obtained from the prior art. The product obtained also had a pale beige color, meaning that no special further decoloration is required.

The enzyme concentrates are usually mixed with a polydiol in order to improve the storage stability. However, such enzyme solutions with polydiol are often black or brown in color, necessitating decoloration prior to further processing in detergents and cleaners.

Table 2

	t = 0	60 min	90 min
Microemulsion 1	100	100	100
Microemulsion 2	100	96	91
Microemulsion 3	100	72	70



**Patent claims**

1. A process for the preparation of microencapsulated enzymes, in which an aqueous enzyme solution and a starch solution or starch emulsion are mixed together and the enzyme solution is dispersed in the starch solution or starch emulsion.  
5
2. The process as claimed in claim 1, wherein the starch is chosen from hydrophobicized starches.  
10
3. The process as claimed in either of claims 1 and 2, wherein the enzymes are chosen from at least one of protease, amylase, lipase and cellulase.  
15
4. The process as claimed in any of claims 1 to 3, wherein the aqueous enzyme solution is an enzyme concentrate originating from fermentation.
- 20 5. The process as claimed in any of claims 1 to 4, wherein the resulting dispersion is subjected to spray drying.
- 25 6. The use of the low-water enzyme preparation as claimed in any of claims 1 to 5 in detergents and cleaners.
- 30 7. The use as claimed in claim 6, wherein the detergents and cleaners are liquid to gelatinous bleach-containing detergents and cleaners.
- 35 8. A detergent or cleaner comprising surfactants and builder substances, and optionally further customary ingredients wherein microencapsulated enzymes obtained by any of claims 1 to 5 are used.
9. The composition as claimed in claim 8, which is a liquid to gelatinous detergent or cleaner.

10. The composition as claimed in either of claims 8 and 9, which comprises a bleach.
- 5 11. The composition as claimed in any of claims 8 to 10, which further comprises sequestering agents, electrolytes, pH regulators and further auxiliaries, such as optical brighteners, anti-redeposition agents, color-transfer inhibitors, 10 foam regulators, additional bleach activators, dyes and fragrances.
12. The composition as claimed in any of claims 8 to 11, which comprises from 0 to 20% by weight of 15 anionic surfactants, 40 to 80% by weight of nonionic surfactants, 2 to 25% by weight of builder materials, 0 to 20% by weight of bleaches, 0 to 20% by weight of bleach activators, 0 to 5% by weight of enzymes, fragrances and further 20 ingredients.